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14. ABSTRACT

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THERMAL CHARACTERIZATION AND PROCESS MODIFICATION OF AN RTM EPOXY RESIN

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ABSTRACT

The Materials and Structures Divisions at the Naval Air Systems Command have teamed together along with industry to demonstrate to a high level of confidence the viability of an agile resin transfer molding (RTM) manufacturing process, also known as intelligent processing. Utilizing fabrication, analysis, modeling and testing efforts, this program will provide an assessment of the Northwestern University's advanced injector system. This paper's objective is to thermally characterize the selected SI- ZG-5A epoxy resin, formulated by A.T.A.R.D. Laboratories. This analysis consists of a comprehensive program of resin characterization and cure modeling. Modulated Differential Scanning Calorimetry (MDSC), rheology measurements and thermogravimetric analysis (TGA) were used to determine the cure kinetics, glass transitions, processing temperature and volatiles during cure. The manufacturer's recommended cure cycle was followed in order to establish a reference glass transition (T_g), enthalpy of cure and gel point during cure. Once this analysis was complete, variations of the cure cycle were performed in order to determine if the cure cycle could be modified. Cure kinetics were also determined using the variable heating rate method. In conclusion, the SI-ZG-5A resin system has been found to be a robust RTM resin by being forgiving of process variations. However, the effect of these variations on final mechanical properties is still being determined.

KEY WORDS: Thermal Analysis, Resin Transfer Molding, Kinetics

INTRODUCTION

The Polymers and Composites Branch of the Naval Air Systems Command (NAVAIR), have joined with government and industry partners in support of the Northwestern University (NWU) Advanced Materials Intelligent Processing Center (AMIPC) program. The objective of this work is to demonstrate agile manufacturing, also known as intelligent processing, of composite materials. This is to be achieved by improving Resin Transfer Molding (RTM) using automation. In-house research has focused on evaluations of the technologies developed by the Center to better understand the bounds of intelligent processing as it applies to current and future naval aircraft.

RTM offers significant potential for the fabrication of naval aircraft components. The potential benefits of an RTM process include highly accurate, complex-shaped parts and reduced cost than autoclave processes. Today, however, resin transfer molding is used to fabricate only a small number of naval aircraft components. Each of these components is infiltrated with a one-part resin system to remove the need to meter and

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mix resins, catalysts, and accelerators during manufacturing. This approach simplifies the overall manufacturing process by reducing the number of parameters that must be controlled. However, few aerospace resin systems can be premixed and their costs tend to be high. In addition, aerospace resins tend to have short out times and high viscosity, leading to pumping and mold-filling issues. Additional obstacles to implementing RTM in the past include poor part-to-part consistency and reliability, as well as the operator expertise required.

Recent improvements in RTM equipment and technology allow increased control and repeatability of material metering, mixing, and delivery [1]. These improvements open the door to the possibility of low-cost, aerospace-quality naval aircraft components using multi-part resin systems. This new technology promises much improved flexibility in terms of RTM'able resin systems in the future. However, this technology is not without negative aspects including higher waste and the potential of discharging the several components. The chemistry can be very complicated and the proper formulation of these systems is still often regarded as proprietary information [2]. Our work at NAVAIR seeks to evaluate the capability of cutting edge resin injection equipment for multi-component resin systems as well as evaluate the risks associated with improper usage or control, we are specifically looking at an automated equipment system built by Northwestern University as part of the AMIPC program.

NAVAIR Materials has several objectives in support of the AMIPC program. One goal is to evaluate the design and performance of the Northwestern University (NWU) advanced resin injection system. A second goal was the selection and evaluation of materials and processes for study utilizing the NWU system. This includes the determination of composite cure kinetics for these chosen materials. By understanding the cure kinetics, the appropriate process parameters can be determined and included in the process. A third goal is to manufacture aerospace quality panels utilizing the selected resin systems and the NWU system. Future work will verify the composite mechanical strength with changes in the mix ratios [3].

This paper discusses work performed in support of the resin characterization and cure modeling. The primary resin system selected for study was a two-part epoxy resin system, SI-ZG-5A, by A.T.A.R.D. Laboratories. It was selected for evaluation based in part on prior experience with other AMIPC partners [4]. This system was advertised to have properties similar to leading epoxy systems, with the added benefit of additional flexibility in processing. Thermal analysis techniques performed on this resin system include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and rheometric dynamic analysis (RDA).

MANUFACTURER'S CURE CYCLE

The manufacturer's recommended cure cycle for SI-ZG-5A consists of an isothermal hold at 65° C for 4 hours, ramp heating of 0.54° C/min to 176° C, followed by a hold for 6 hours [5]. Cure cycle development is often quite arbitrary, such as specifying a process to fit into existing specifications to allow for "drop-in" replacement of an older resin system. However, these selected cure cycles are not necessarily optimized to allow for shortest processing time, lower temperatures, or best part quality. As a result, thermal analysis was performed on the SI-ZG-5A epoxy resin to see if the manufacturer's cure cycle could be optimized for intelligent processing.

DSC was performed on the TA Instrument model 2920. Figure 1 is of a DSC thermogram showing the temperature-time profile of this cure. The cure shows that the main exotherm for cure occurs during the ramp between 65 to 176° C. The glass transition temperature (T_g) was found to be 207° C after the manufacturer's cure cycle was completed.

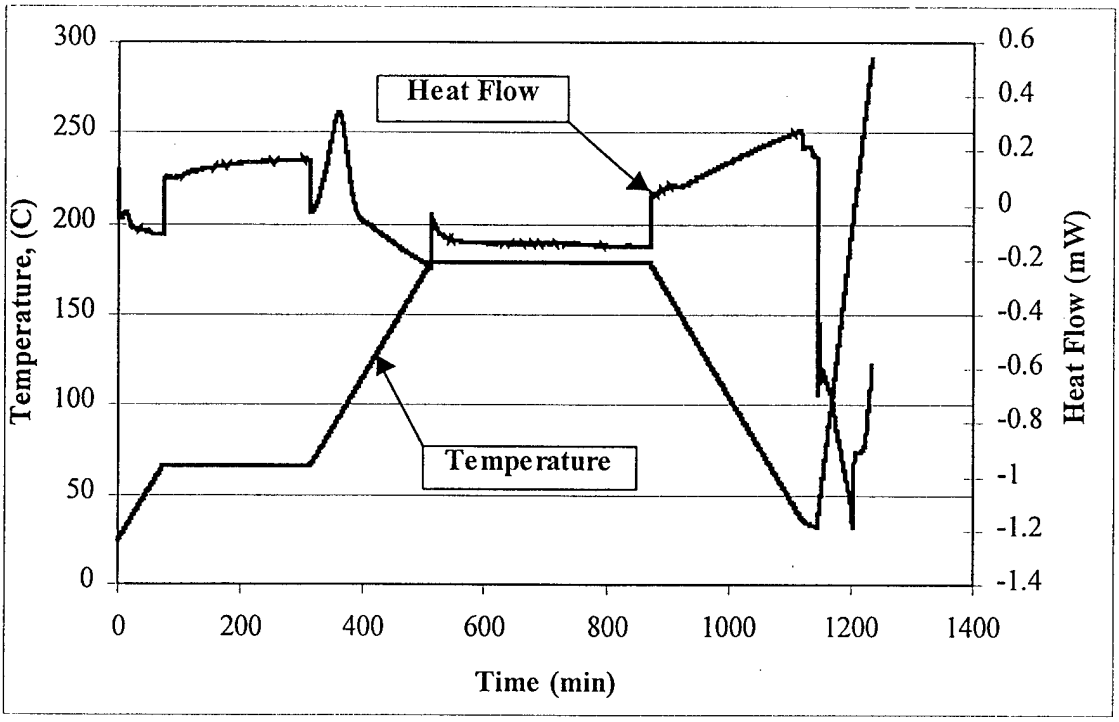

FIGURE 1. DSC curve of A.T.A.R.D. SI-ZG-5A epoxy resin cure cycle.

The rheology profile for the resin was determined using the Rheometrics Scientific RDA II analyzer. The uncured resin was placed between two 25-mm aluminum parallel plates with a gap setting of 0.8 mm. The plates were oscillated at 1 Hz frequency while a constant 10% strain was applied. Figure 2 shows this viscosity profile. Minimum viscosity occurs in 79 minutes at 2.3 cP and gel occurs at approximately 4 hours. During the cure, thermogravimetric analysis showed a 3% weight loss. Further experiments showed that this weight loss was due to the volatility of the catalyst.

TABLE I. Glass Transition Temperature values with respect to cure cycle modification.

Cure Time (hrs) at 176° C	T_g (°C)
6 (manf. rec. cure)	208
4	206
3	205
2	201

Modifications in the manufacturer's cure cycle were studied to determine if the hold temperatures at 65° C and 176° C could be reduced or eliminated. During this task

the initial hold for 4 hours at 65° C was eliminated. The samples were placed in the DSC cell pre-heated at 65° C and immediately ramped at 0.54°C/min to 176° C. The hold temperature time was reduced from the manufacturer's 6 hour hold to 4 hours, 3 hours, and 2 hours. Reduction in the hold time at 176° C had little affect on the glass transition temperature. Reducing the hold time by 2 hours shifted the T_g only 2° C, while a further 1 hour reduction resulted in another 1° C decrease and finally reducing the hold time to 2 hours produced a T_g of 201° C (complete results are listed in Table I.)

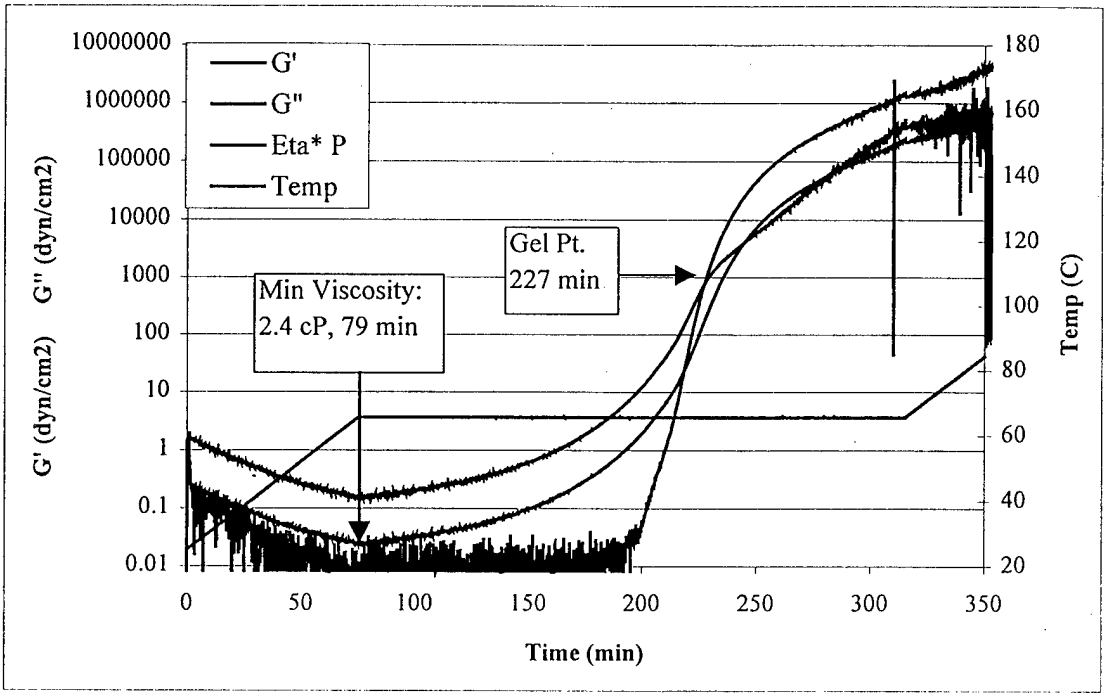

FIGURE 2. Resin viscosity profile of the A.T.A.R.D. SI-ZG-5A epoxy resin system.

Finally, variations in the resin mix ratio were made to see the effect on cure times and change with T_g. Changing the mix ratio to 55/45 part A to B, had no appreciable effect on the gel point time or glass transition. While changing the mix ratio to 45/55 A to B, increased the glass transition to 211° C which indicates an increase in cross-linking, the gel point likewise showed an small decrease in time. Table II shows the change in glass transitions temperature as the mix ratios are varied. At either extreme we were unable to detect a glass transition temperature, since the resin never properly cures, at the one extreme the catalyst is used up leaving too much unreacted monomer, at the opposite extreme there is too much catalyst and the reaction essentially burns itself out prematurely. Future work will explore the effects of varying the mix ratio on the mechanical properties of the composite to determine the range of acceptable error in the automated resin transfer molding process.

TABLE II. Glass Transition Temperature values with respect to mix ratios.

Mix ratios A/B	T_g (° C)
75/25	None detected
60/40	203
55/45	207
50/50	207
45/55	211
40/60	224
35/65	228
25/75	None detected

KINETIC METHOD

The variable heating rate method [6,7] was employed to obtain cure kinetics data by differential scanning calorimetry (DSC.) This kinetic model established a baseline for comparison of variations of the cure cycle and mix ratios. The heating rates chosen were 0.2, 0.5, 1.0, 5.0, 10.0 and 20.0 °C/min. The equation used to calculate the activation energy was

$$\frac{d\log\beta}{d(1/K)} = 0.457E/R \tag{1}$$

where β is the heating rate, E is the activation energy, R is the gas constant (1.987 cal/mol-K), T is the absolute temperature, and the constant which arose from the assumption of first-order behavior. As suggested by the equation, a plot of the log-heating rate versus the reciprocal of the absolute temperature at a constant conversion will have a slope of 0.457 E/R. The variable heating rate method has been used successfully for obtaining kinetic constants. The accuracy for determining activation energy has been reported to be within +/- 3% [8]. For this analysis, the constant conversion point was taken at the peak exotherm. The Arrhenius frequency factor can be calculated from the equation,

$$A = \frac{\beta E}{RT^2} e^{\frac{E}{RT}} . \tag{2}$$

Once E and A are known, assuming a first order reaction, the rate constant, k, may be calculated from the equation,

$$\ln k = \ln A - \frac{E}{RT} . \tag{3}$$

DSC EXPERIMENTS AND RESULTS

The neat resin was run in a crimped aluminum pan in a nitrogen atmosphere with a flow rate of 50 ml/min. For each heating rate, Indium metal standard was used to calibrate the heat flow and the onset temperature in the DSC cell. Figure 3 shows a typical DSC thermogram at a heating rate 5° C/min for the A.T.A.R.D. SI-ZG-5A epoxy resin. This thermogram shows the curve exotherm occurring at 143°C with an enthalpy value of 393 J/g.

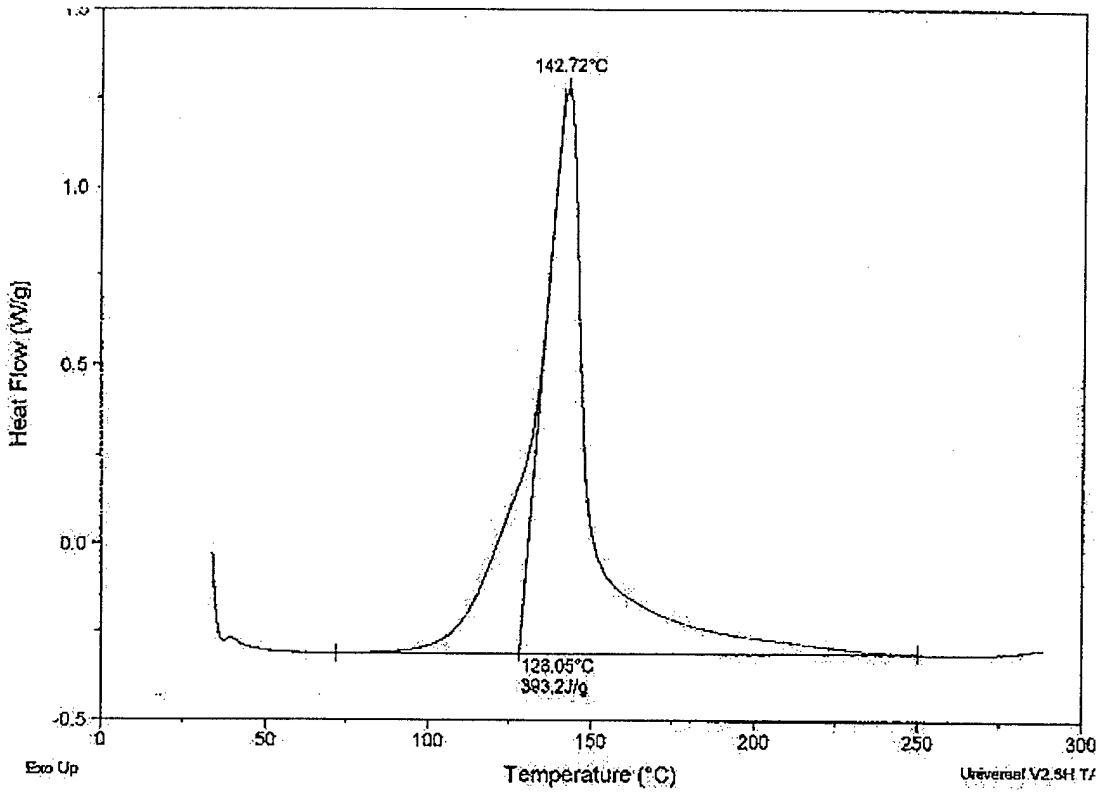

FIGURE 3. DSC thermogram of A.T.A.R.D. SI-ZG-5A epoxy resin at 5° C/min.

TABLE III. Variable heating rate data of uncured A.T.A.R.D. SI-ZG-5A resin.

HEATING RATE (° C/min)	PEAK HEIGHT (° C)	ENTHALPY (J/g)
0.2	86.8	272
0.5	100.1	298
1.0	113.5	316
2.0	127	373
5.0	143	393
10.0	158	362
20.0	175	288

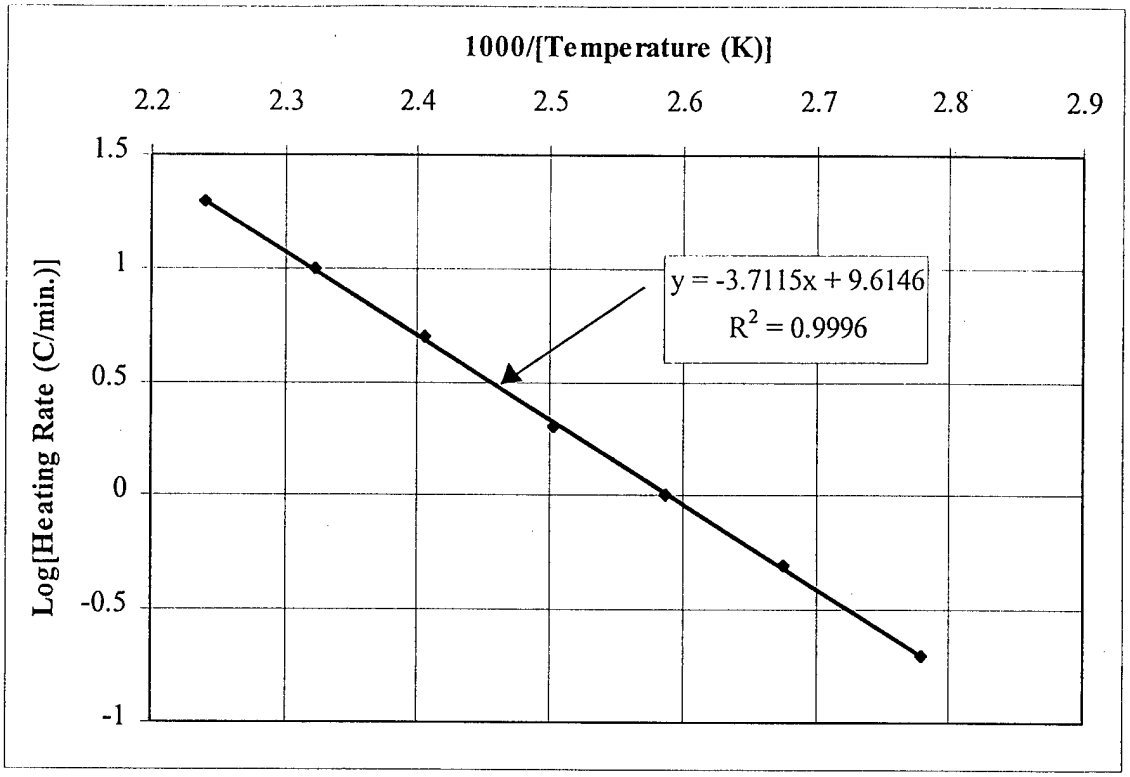

FIGURE 4. Arrhenius plot from the variable heating rate scans.

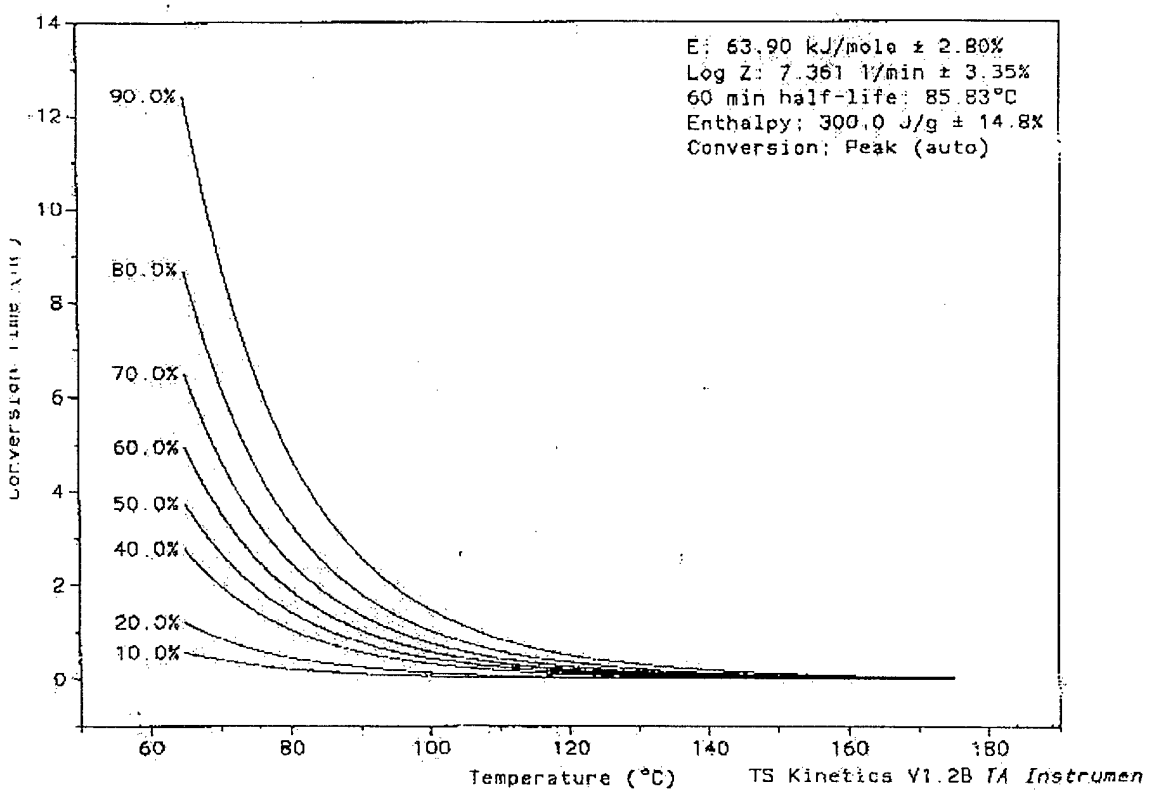

FIGURE 5. Plot of the predicted conversion time versus temperature.

As the heating rate increases the exothermic cure peaks shift to higher temperatures this is the base for the kinetic model. Table III lists the heating rates with their associated peak heights and total enthalpy values. Figure 4 is the Arrhenius plot for the seven heating rates used. The straight line indicates that their is good agreement with the assumption of the first order behavior. From Figure 4, the activation energy was found to be 63.9 kJ/mol and the log Arrhenius frequency factor was found to be 7.361 (1/min).

By utilizing the rate constant, percent conversions were calculated. Figure 5 illustrates the predicted conversion time versus temperature based on the kinetic model. For example, 50% conversion is achieved at 4 hours at 65°C. This conversion corresponds with the gel point found with the rheology analysis. Other conversions found at 65° C are 20% in 1 hour and 60% in 8.5 hours. At 135° C, 50% conversion occurs in less than 5 min. These conversion times and temperatures will be used to modify the cure process by predicting parameters such as gel times. The parameters can also be used to determine important process parameters such as when to apply pressure for the autoclave cure method or how fast to inject the resin and at what temperature for the resin transfer molding process.

The model shows that the gel time (50.0% conversion) at 65° C would occur in approximately 4 hours. This prediction agrees with the analysis found from the rheology experiment, which the gel time occurred, in 227 min (~ 4 hours).

SUMMARY

The manufacturer's cure cycle recommended an isothermal hold at 65° C for 4 hours, ramp heating to 176°C and hold for 6 hours. The thermal analysis revealed that eliminating the initial temperature hold and also reducing the hold time at the final temperature by one third could be done without any significant changes in thermal properties. These changes can be incorporated to modify the processing of the SI-ZG-5A epoxy resin.

The cure kinetics analysis reveals that predicted gel time did agree with the manufacturer's cure cycle recommendation for time to gel. This will allow for future cure cycle modifications in order to shorten the cure time process.

Mix ratios were varied showing that the resin system is robust enough to allow mix ratio changes without significant glass transition temperature change. The resin system can allow for mix changes if there is a malfunction or error with one or both of the RTM mixing pumps. This finding can permit the continuing of the RTM process when the operator knows there could be an error without the loss of work time and retooling. Future work will verify the composite mechanical strength with changes in the mix ratios.

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